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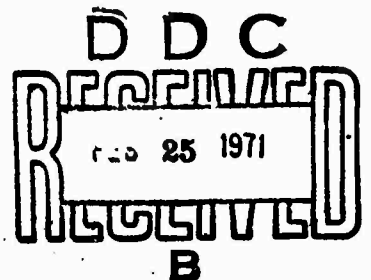
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1.0 Experimental Studies of Thin-Film Switching

Personnel: Floyd O. Arntz, Bimal P. Mathur

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An rf sputtering facility which will permit preparation of a wide variety of films has been built and is used for preparation of all chalcogenide films studied in this program. The facility consists of two vacuum systems, two stable rf supplies (100 watt, 500 watt), a number of interchangeable stainless steel sputtering chambers of 8 inch diameter and 10 inch height, and for support of the latter a console containing gas flow controls, pressure sensing electronics, a recycling water cooling system for the targets and rf matching networks. In addition quartz crystal monitoring of deposit thickness has been provided for and shall be installed shortly.

We have developed a procedure for producing one inch diameter disc-shaped sputtering targets by solidification in evacuated quartz ampules. These solid fused targets are produced in thicknesses of one to four mm and are mounted as-grown onto metal support plates with a thermally conducting silver loaded epoxy. We believe such targets are quite homogeneous except for a very thin surface layer and therefore require little presputtering at low power densities is necessary to produce homogeneous films with hot pressed fused glass powder targets.¹

Preliminary to investigation of dynamic strain effects we have engaged in study of the influence of static strain on switching of films deposited upon PZT-4 ceramic piezoelectric transducers. In such films switching has proven sensitive to strain but not in a predictable or necessarily reversible manner. We believe this is due to complications associated with development

of the crystalline phase normally identified with the high conductivity state of memory switches. Indications are that development of films reliably exhibiting threshold switching action and remaining amorphous when subject to such strains may require substantial effort during the second half year of this contract period. However we expect films satisfying these requirements would also be more reliable in other respects and would be less sensitive to the choice of substrate.

Chalcogenide films for most of our work are now processed by integrated circuit photolithographic techniques. Prior to deposition of the chalcogenide film small windows, commonly 50 μm in diameter, are etched through a sputtering 500 \AA - 1000 \AA SiO_2 film to an underlying molybdenum contact layer. After deposition of the chalcogenide a Mo film is rf sputtered to form the top contacts. Electrical isolation of individual devices is accomplished by photolithographic metal etching of this structure which results in an array of 0.5 mm diameter Mo electrodes contacting the chalcogenide film. We have found that when such devices exhibit deterioration of electrical switching properties the Mo electrodes often show slight microscopic visible deterioration at the perimeter of the windows. We intend to substitute other dielectrics for the SiO_2 and shall overcoat the top Mo contact film in an attempt to discriminate against this effect.

2.0 Studies of Bulk Memory-Type Material

Personnel: David Adler, Eric L. Prael, Stephen D. Senturia

2.1 Effective Charge of Ions in Chalcogenide Glasses

The Te^{125} NMR experiments² carried out on amorphous and crystalline TeGe alloys has been compared with similar measurements on PbTe and SnTe³ in order to obtain an estimate of the effective charge on Te ions in the amorphous chalcogenides.⁴ It was concluded that the effective charge of a Te atom with two Te nearest neighbors is close to zero, that of a Te atom

with one neighboring Ge atom is $-0.18e$, and that of a Te atom with two neighboring Ge atoms is $-0.35e$. These relatively small values for effective charge in the chalcogenide glasses make it unlikely that a field-induced ferroelectric-type displacement can account for the observed switching properties. The results should prove extremely useful in reanalyzing the x-ray diffraction experiments to obtain the structure of such alloys.⁵

2.2 NMR and EPR Studies of Memory-Type Material

In order to investigate the density of unpaired spins in the two states of memory-type chalcogenide glasses, attempts are being made to measure the spin-lattice relaxation time of the Te^{125} nuclear magnetic resonance. Previous indications from Knight shift measurements² were that these times are quite long, due to a large density of unpaired spins in both states. The equipment for this project has been constructed, and experiments will begin shortly. Electron paramagnetic resonance experiments will also be performed to shed further light on the unpaired-spin density, a critical theoretical parameter, although short relaxation times could lead to a null result.

3.0 Composition Dependence of Switching Parameters

Personnel: Richard Ku

The effects on the switching parameters of substituting Se for Te in some bulk memory-type chalcogenide glasses have been systematically investigated. In particular, the system $\text{As}_4 \text{Ge}_{16} (\text{Te}_{1-x} \text{Se}_x)_{80}$ has been studied in detail. The glass with $x=0$ had previously been shown to be an excellent memory-type material, the switching being completely reversible and the conducting state resulting primarily from regions of As-doped crystallized Te .⁶ Except for the regions near $x=0.5$, no difficulty in producing homogeneous bulk glasses was encountered. However, good memory switching was obtained

only near $x=0$. The region $0.1 < x < 0.3$ provided threshold switching with an increasing threshold voltage and relatively poor dc stability. The material could be thermally crystallized by an annealing technique, but was then quite inhomogeneous and possessed a resistivity two orders of magnitude higher than the crystallized state at $x=0$. For $x > 0.6$, the threshold field had increased sufficiently so that no electrical switching was obtained up to 400V. These results are consistent with the hypothesis that doped, crystalline Te is primarily responsible for the high conductivity memory state.⁶ Since Se is a wide gap semiconductor and has a much higher crystallization temperature than Te, substitution of Se for Te should indeed have deleterious effects on the switching process.

4.0 Properties of Crystalline and Amorphous Si_2Te_3

Personnel: Ulrich Birkholz, Kurt E. Petersen

In order to compare the properties of crystalline and amorphous phases of a low-mobility semiconductor, the material Si_2Te_3 is being investigated in detail. Si_2Te_3 is the only known compound in the Si - Te system. Single crystals have been prepared by vacuum sublimation in a temperature gradient near 750C; the crystals are red transparent platelets, of thickness between 50 μm and 10 μm , and the results indicate an optical gap of 2 eV. The gap exhibits a blue shift of approximately 1 meV/K as the temperature is lowered. No photoluminescence appears in the vicinity of the optical gap, but a broad peak appears near 1.3 eV. This is consistent with observations on arsenic chalcogenides.

Rf sputtered films of amorphous Si_2Te_3 have been prepared. Bulk amorphous Si_2Te_3 crystallizes at 400C, but annealing of the sputtered films at 350C is sufficient to induce crystallization. The optical and electrical properties of amorphous and crystalline films will be investigated and compared.

5.0 Theoretical Studies of Amorphous Semiconductors

Personnel: David Adler, Floyd O. Arntz,

Kathryn Kanarek, Theodore Kaplan

5.1 Band Structure of Amorphous Semiconductors

A comprehensive review of all theoretical and experimental work on amorphous semiconductors is nearing completion.⁷ Such a compilation focuses on the large gaps in our knowledge and the mass of work that still needs to be done. Nevertheless, much progress has been made in refining the basic band model recently proposed for covalent amorphous semiconductors.⁸ A qualitative procedure for taking into account the effects of electronic correlations and electron-phonon interactions in the band tails of amorphous semiconductors has been proposed.⁹ The resulting quasiparticle spectrum has many of the same features as appear in the simple one-electron approximation, but two important modifications must be introduced. Electronic correlations split the localized states in the valence-band tail into two quasiparticle bands, the splitting being of the order of tenths of an eV. On the other hand, localized states in the conduction-band tail are also pushed up in energy relative to the valence-band mobility edge, so that the redistribution of electronic states takes place much as Cohen *et al.*⁸ predicted. The effects of the electron-phonon interaction partially compensate for correlation effects, since ionic distortions around localized electrons reduce the energies of the localized states relative to those of the extended states. This model predicts a significant density of unpaired spins in both the amorphous and crystallized phases of the memory-type chalcogenide glasses presently under experimental investigation (see 2.2).

5.2 Mechanisms for Threshold Switching

The various mechanisms proposed for threshold switching in amorphous materials have been classified and critically analyzed.¹⁰ It is clear that no model yet proposed is completely consistent with the available data, and that electronic as well as thermal effects are important.

Previous thermal models have been inconclusive because they are intrinsically one-dimensional, while the real problem is three dimensional. A fully three-dimensional model, which explicitly takes into account both radial and axial heat flow, is presently under investigation. Steady-state solutions show that if no electronic effects are considered and conductivity increases with temperature in the normal manner, no thermal filaments can arise, primarily because of the high thermal conductivity of the electrodes and the nature of the temperature variation of the conductivity. On the other hand, the addition of even minor electronic effects such as small space-charge regions or slight non-ohmic conductivity can readily lead to development of filamentary conduction. Time-dependent solutions are also being investigated. Preliminary results indicate a small temperature rise prior to breakdown, a large threshold field in the thinner films, a hot central filament and an environment that cools considerably after breakdown. These results agree well with the experimental results on thicker ($>6\mu\text{m}$) films, but tend to disagree with the observation on thinner ($\sim 1\mu\text{m}$) films. Electronic effects appear to be significant for switching in thin films.

5.3 Mechanism for Optical Memory Switching

A model has been proposed to account for the unusual result that several chalcogenide alloys can be changed from the crystalline to the amorphous phase and back again by use of a laser pulse of the same intensity

and duration.¹¹ A combination of the effects of photocrystallization and the differences in absorption of laser radiation between the two phases can explain the experimental results in a simple manner. The effect can be used as a device for bulk storage of information by purely optical techniques.

6.0 Thermal Effects in Amorphous Semiconductor Switching

Personnel: David Adler, Floyd O. Arntz

Terry Holcomb, Edward J. Sokolowski, Jr.

The dependence of switching parameters on temperature is being studied down to 4K in order to test the feasibility of use of memory-type chalcogenide alloys, recently shown to become superconducting in the ON state,¹² as insulator-superconductor switches. An experiment is also being attempted to measure the radial temperature distribution in the ON state of a threshold switch by means of a liquid-crystal sensor. If successful, the results of this experiment will help discriminate between the thermal and electronic models for switching, discussed in 5.2.

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Summary

The rf sputtering is complete and high-quality films are being prepared by integrated circuit photolithographic techniques. The films have proven very strain sensitive and somewhat sensitive to variations in composition. The effective charge of the ions in the amorphous state has been determined from our previous NMR results. More detailed NMR experiments and EPR experiments are being planned, in order to test the recent theoretical models. Amorphous and crystalline Si_2Te_3 films have been deposited in preparation for a comparison of their electrical and optical properties. Thermal effects at low temperatures and the radial temperature distribution of a threshold switch in the ON state are being investigated. A review of recent work in the field is nearing completion, and a review of the possible switching mechanisms has been completed. The basic band model for amorphous semiconductors has been generalized to include electron-electron and electron-phonon interactions. Accurate solutions of the thermal model for switching have been obtained and an explanation for optical switching has been proposed.